
Minerals

Their Constitution and Origin

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Minerals and human health

Introduction

Mineralogy and its methods of investigation are finding increasing use in medicine and in environmental health applications. There are many examples where biologists, physicians, pharmacists, and environmental health professionals rely on the expertise provided by mineralogists. On the one hand, minerals may constitute health hazards. Exposure to asbestos, toxic waste from mining operations, or radiation due to radioactive decay may cause cancer or other diseases. On the other hand, minerals such as salt and calcium are essential nutritional components and, as we have seen in Chapter 23, both bones and teeth are composed of mineral-like crystals.

Minerals are also extensively used in beauty and grooming products. For example, talc is an important ingredient of many cosmetic products, baby powder being one of the better known ones. Minerals such as kaolinite, smectite, nontronite, biotite, and hectorite clays are used in cosmetics, toothpaste, and pharmaceuticals, while mica provides the sheen in lipstick. Most consumers are generally unaware of most of these mineral ingredients.

In this chapter we will explore some of the aspects of minerals related to human health, in both positive and negative ways. In so doing, we will see that our overall health and well-being is intimately connected with the world of minerals.

Mineral-like materials in the human body

The principal mineral-like compounds in humans are phosphates, but other mineral-like crystals occur as well (Table 33.1). Bones of adults consist of approximately 70% calcium phosphate and 30% organic matter. Calcium phosphate forms tiny prismatic crystals less than 1000 Å in length, with a structure and composition similar to that of apatite (Ivanova *et al.*, 2001). Organic matter contains combinations of different collagens, fats, and proteins. The apatite crystallites line up in chains and, together with organic material, form fibers of bone tissue. A portion of the phosphate material of newborns is amorphous. As a child grows, the amorphous material and the existing crystals increase in size. At the same time the portion of organic material decreases with age, with the result that the fibers lose their elasticity and the bone tissue becomes more brittle.

Recent investigations with high-voltage electron microscopic tomography revealed structural relationships between collagen fibers and apatite crystallites (Landis *et al.*, 1996). For example, the crystals in an embryonic chicken bone are only 800 Å × 300 Å × 80 Å (Figure 33.1a), the largest dimension being along the *c*-axis of the hexagonal mineral. A computerized reconstruction indicates that apatite *c*-axes are parallel to the long axis of the collagen fibers and connect the fibers. Furthermore, they are stacked in a regular pattern (Figure 33.1b).

Table 33.1 | Mineral-like substances in the human body

Name	Paragenesis	Place
Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	—	Bones, teeth, kidneys, urinary bladder, salivary glands, prostate, lungs, heart, blood vessels
Brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Apatite, whitlockite	Bones, teeth, kidneys, urinary bladder, prostate
Struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	Whewellite, weddellite, newberyite, apatite	Kidneys, urinary bladder, teeth
Newberyite $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Struvite, apatite	Kidneys, teeth
Whitlockite $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$	Apatite, brushite	Bones, teeth, kidneys, urinary bladder, prostate
Calcite CaCO_3	Apatite, Holesterine	Gall bladder Teeth, salivary glands, tumors, kidneys, lungs
Whewellite $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	Weddellite, apatite, struvite, urinary acid	Urinary bladder
Weddellite $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	Whewellite, apatite, struvite, urinary acid	Urinary system
Urinary acid $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$	Whewellite, weddellite, struverite, apatite	Urinary system

Note: From Katkova, 1996.

Biogenic apatite-like minerals have a rather variable composition, which can be expressed approximately by a formula such as $\text{Ca}_{10-x}(\text{PO}_4)_{6-y}(\text{CO}_3)_z(\text{OH})_{2+w} \cdot n\text{H}_2\text{O}$. A number of PO_4^{3-} tetrahedra in the structure are replaced by $\text{CO}_3\text{OH}^{3-}$ or CO_3^{2-} groups. The main crystalline phase in cartilage is also biogenetic phosphate, analogous to apatite and constituting about 5% of the volume. Modifications of apatite form 96% of tooth enamel (the outer coating of teeth) and 70% of dentine (the material beneath the enamel), with the rest of tissue volume composed of proteins. In tooth enamel, some OH^- is replaced by F^- , which makes teeth more resistant to decay. In enamel, crystals are organized in a layered structure to improve mechanical properties (Figure 33.2, see also Figure 23.6).

Crystals may also grow abnormally within the human body. Aggregations of biogenetic apatite up to 2 cm in size have been discovered in some malignant tumors. The lungs of patients with tuberculosis show calcification, with apatite and whitlockite ($\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{PO}_3\text{OH}$) having been observed. Similarly, in people with heart disease, heart tissue, including arteries and the aorta, can become covered with apatite-like calcium phosphate crystals (Figure 33.3).

Abnormal “stones” form in the bladder, kidneys, liver, gall bladder, and trachea, and are composed of amorphous or very diverse crystalline phases of phosphates, carbonates, oxalates, or urates (Table 33.2). The morphology of the stones resembles inorganically formed concretions, with rhythmical zoning, geometrical

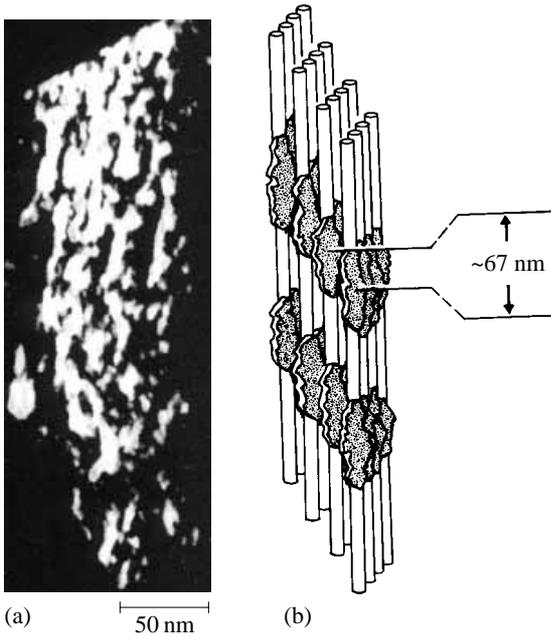


Fig. 33.1 (a) Tomographic reconstruction of apatite crystallites in bone from an embryonic chicken, based on high-voltage electron micrographs. Note the alignment of irregularly shaped, platy crystals. (b) Model of the relationship between apatite platelets and collagen fibrils with a regular stacking, based on the tomographic evidence (after Landis *et al.*, 1996).

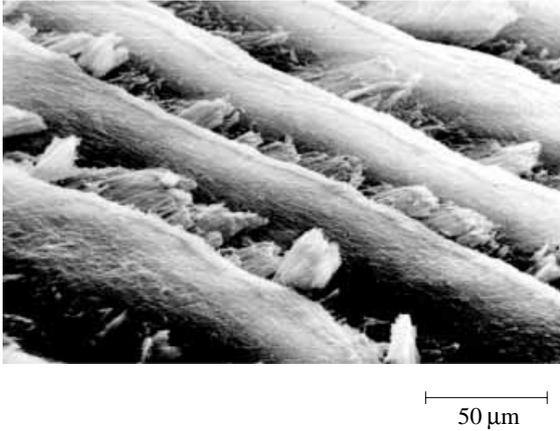


Fig. 33.2 SEM image illustrating the layered structure of prismatic apatite crystals in enamel from human teeth (courtesy V. T. Wright, University of North Carolina, Chapel Hill).

sorting, and subgrain formation. In some cases a drusy growth has been documented.

Minerals in nutrition

Apart from table salt, known by mineralogists as halite (NaCl), minerals are rarely consciously ingested by humans. Among the exceptions are barite (BaSO₄), called by the Russian mineralogist A.E. Fersman “the most edible mineral”, which is used as an inert filling of chocolate, and kaolinite, which is added to some ice creams to provide consistency when they start to melt. There are also other examples, less well known, where minerals are part of our food. Yet on shelves in supermarkets, “minerals” in the form of nutritional additives play a role almost as important as that of vitamins, and in every modern book

on nutrition there is a chapter on minerals. This popularity is in part due to the rather free use of the term “mineral” by physicians, pharmacists, and nutritionists. Traditionally they call any inorganic compound “mineral”, following an old usage that divided chemistry into two branches: organic and mineral.

In nutrition, so-called minerals are divided into macrominerals (calcium, chlorine, magnesium, phosphorus, potassium, sodium, and sulfur) and microminerals (such as chromium,

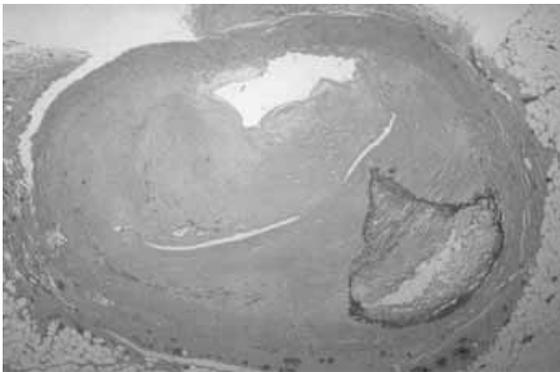


Fig. 33.3 Micrograph displaying a section through a human coronary artery. The dark region (right side) is calcified tissue that is common in arteriosclerosis (courtesy E. C. Klatt, Florida State University, College of Medicine).

Table 33.2 | Composition of urinary and gall stones

Medical name	Mineral name	Urinary	Gall	Formula
Oxalates	Whewellite	X		$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
	Weddellite	X		$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Phosphates	Struvite	X		$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$
	Apatite	X	X	$\sim \text{Ca}_5(\text{PO}_4, \text{CO}_3, \text{OH})_3(\text{OH})$
	Newberryite	X		$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	Brushite	X		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	Whitlockite	X		$\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$
Carbonates	Vaterite	X	X	CaCO_3 hexagonal
	Calcite	X	X	CaCO_3 trigonal
	Aragonite		X	CaCO_3 orthorhombic
Oxides	Magnetite	X		FeFe_2O_4
	Hematite	X		Fe_2O_3
	Goethite	X		FeOOH
	Lepidocrocite	X		FeOOH
Urates	Urea	X		$\text{C}_5\text{H}_4\text{N}_4\text{O}_3$
	—	X		$\text{C}_5\text{H}_4\text{N}_4\text{O}_3 \cdot 2\text{H}_2\text{O}$
	—	X		$\text{C}_5\text{H}_2\text{O}_3\text{N}_4(\text{NH}_4)_2$
	—	X		$\text{C}_5\text{H}_2\text{O}_3\text{N}_4\text{Na}_2 \cdot \text{H}_2\text{O}$
	—	X		$\text{C}_5\text{H}_2\text{O}_3\text{N}_4\text{Ca} \cdot 2\text{H}_2\text{O}$
Organic compounds	Holesterine		X	$\text{C}_{27}\text{H}_{46}\text{O}$
	Holesterine, hydrous		X	$\text{C}_{27}\text{H}_{46}\text{O} \cdot \text{H}_2\text{O}$
	Ca-palmaniate		X	$\text{CH}_3(\text{CH}_2)_{14}(\text{COO})_2\text{Ca}$

Note: X indicates positive association.

Source: From Katkova, 1996; Korago, 1992.

cobalt, fluorine, iron, manganese, molybdenum, and zinc). The former are required in rather large quantities in our daily diet, while the latter are also essential for physiological functions, but only in trace amounts. Table 33.3 lists some of the physiological functions of macro- and micro-minerals. Ultimately most of these elements are derived from “real minerals”, but indirectly through a long chain of natural events. Primary minerals in rocks decompose to clay minerals that become part of soils. Plants growing on those soils accumulate the inorganic elements and store them in roots and leaves. Animals eat the plants and transfer the elements into their tissue, and finally humans acquire these elements largely by consuming either plants or animals.

The quantity of elements stored in plants is considerable, particularly in the green parts (e.g., average contents on a moisture-free basis in some legumes and grasses are Ca 1–4 weight%, P 0.1–0.5 weight%, Fe 100–200 ppm, Cu 5–15 ppm). These amounts vary greatly with the mineral content of the soil, but they are also affected by many other factors such as climate and elemental balance. The mineral content of plants can have a direct effect on the health of animals. It has been observed that cattle grazing in pastures with underlying limestone are less likely to develop bone diseases than those grazing on granitic soils. The trace element selenium, an essential antioxidant to preserve the cellular membrane, can become toxic if concentrations are too high, as in some sedimentary

Table 33.3 | Essential nutritional elements and their physiological functions

Physiological functions

Macrominerals (required in large amounts)

Ca	Bones, teeth, neural transmission, muscle functions
Cl	Water and electrolyte balance, digestive acid
Mg	Regulating chemical reactions, nerve transmission, blood vessels
P	Bones, cell functions, and blood supply
K	Growth, body fluid, muscle contraction, neural transmissions
Na	Regulating acid–base balance, neural transmissions, blood pressure
S	Constituent of proteins, thiamine, structure of hair, skin

Microminerals (required in trace amounts)

Cr	Glucose metabolism
Co	Vitamin B12, red blood cells
Cu	Red blood cells, prevents anemia, nervous system, metabolism
F	Tooth decay, strong bones
Fe	Hemoglobin, immune system
I	Thyroid hormones, reproduction
Mn	Tendon and bone development, central nervous system, enzymatic reactions
Mo	Growth, enzymes
Se	Prevents cardiovascular disease, cancer, detoxifies pollutants, antioxidant
Zn	Enzymes, red blood cells, sense of taste/smell, immune system, protects liver

Source: From Dunn, 1983.

rocks. Conversely, a lack of selenium in the diet of endangered Bighorn Sheep was recently implicated in the low survival rate of newborn lambs. In human nutrition, calcium, magnesium, phosphorus, and copper are stored in legumes, whereas chromium, iron, manganese, and zinc are enriched in cereals.

A number of drugs used in the treatment of internal and external diseases contain minerals. The halide mineral bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), for example, is used for treating arthritis and rheumatic fever. Calcite, dolomite and apatite are used as calcium, magnesium, and phosphorus supplements.

Direct ingestion of soils as a food supplement and medicine, known as *geophagy*, is common among some primates and is still practiced in some countries by humans. Ancient Greeks and Romans used tablets of soil as a remedy against poisoning. Traditionally and until fairly recently, soils were consumed in China as famine food. Well into the eighteenth century, clay was mixed with flour in the preparation of bread.

Pomo Indians in northern California (USA) mixed clay with ground acorns to neutralize the acidity. The most widespread incidence of geophagy is in Central Africa, as well as among some African Americans in the southern USA. In Africa geophagic clays are widely used by pregnant women as food supplements containing elements such as phosphorus, potassium, magnesium, copper, zinc, manganese, and iron, and as remedies against diarrhea. Interestingly the chemical composition of these soils and soil extracts is remarkably similar to modern commercial mineral-nutrient substitutes. The main clay mineral in geophagic soils is kaolinite. Soils rich in smectite are less desirable because of their swelling properties (see Chapter 27).

Minerals as health hazards

Diseases caused by particulates

Minerals are ubiquitous in our daily environment. Along with their synthetic analogs, they

are used in household products, as abrasives, pharmaceuticals, catalysts, fillers, anti-caking agents, building materials, insulation, and pigments. We are exposed to minerals daily, often without being aware of it. Many workers, including miners, quarry workers, sandblasters, stone masons, and agricultural workers, are exposed to dust from a variety of sources and inhale small mineral fragments. These workers have an increased probability of developing pulmonary diseases. Since workers are often exposed to dust from a mixture of minerals, it is difficult to establish whether it is the number of ingested particles or a specific mineral that causes a particular disease. Minerals for which a dose-response relationship between the amount of exposure and the degree of injury has been established with some confidence are fibrous forms of amphibole asbestos (riebeckite, trade name *crocidolite*; grunerite, trade name *amosite*; tremolite, actinolite, and anthophyllite), serpentine asbestos (*chrysotile*), quartz, and coal. Recently several other amphibole minerals (winchite, richterite, and arvedsonite) have been implicated as causing cancer in workers at the Libby, Montana (USA), vermiculite mines, and the Environmental Protection Agency is currently reviewing whether the existing asbestos regulations in the USA should be extended to include these minerals. A brief review of these disease-causing minerals and the methods used to assess and monitor their presence is given below.

The first reported case of the lung disease *asbestosis* was in 1927 in a chrysotile textile worker. Ten years later asbestosis became generally accepted by the industry as an occupational disease with distinct characteristics. Stanton *et al.* (1981) demonstrated with a classical, though still controversial, epidemiological study that rats exposed to fibrous asbestos dust developed carcinogenic tumors (Figure 33.4). In the Stanton *et al.* study, rats exposed to equivalent amounts of nonasbestos dust (such as talc) did not develop the diseases. The researchers concluded that the fibrous morphology caused the disease. Since then, much further research has been done, and the fibrous morphology of asbestos has, in fact, been found to be only part of the reason that asbestos is harmful. Numerous other minerals exist

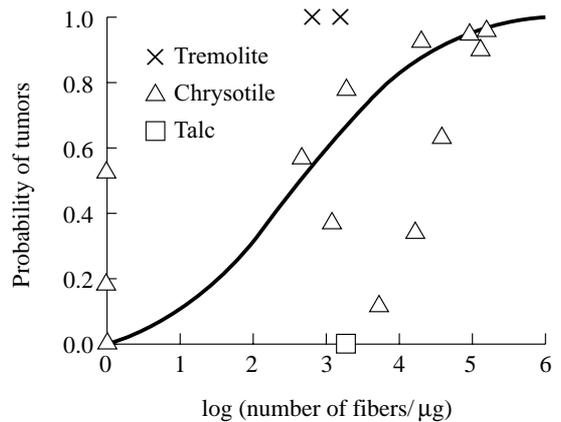


Fig. 33.4 Incidence of malignant tumors in rats as function of fiber concentration (after Stanton *et al.*, 1981).

that can occur in a fibrous morphology, such as talc, gypsum, and clays (i.e., kaolinite, halloysite, sepiolite) but they have not been associated with lung disease. In the early 1980s, the use of asbestos in the USA and in Europe was largely eliminated. However, much asbestos still exists in insulation, fireproofing, flooring, roofing, and surfacing materials of older buildings.

The detailed mechanisms of the lung diseases caused by inhaled dust are still unclear, but it has been established that sustained exposure to asbestos minerals can cause *cancer of the lung*, the trachea, and the bronchial walls. *Mesothelioma* is a rare malignant tumor, correlated with crocidolite exposure. It arises from the mesothelial membrane that lines the pleural cavity. Mesothelioma generally appears 20–40 years after asbestos exposure, but once it appears there is rapid growth, with the tumor spreading and invading adjacent organs such as the heart, liver, and lymph nodes. Death often occurs within one year after the first symptoms appear. *Asbestosis* is a nonmalignant disease that involves interstitial fibrosis with hardening of the lung tissue. It may lead to severe loss of lung function and ultimate respiratory or cardiac failure. The disease is often associated with pleural calcification and the appearance of asbestos bodies consisting of fibers coated with collagen (Figure 33.5). Asbestosis extends eventually to the walls of the alveoli (small air cavities where the oxygen exchange takes place) and leads to the destruction of alveolar spaces.

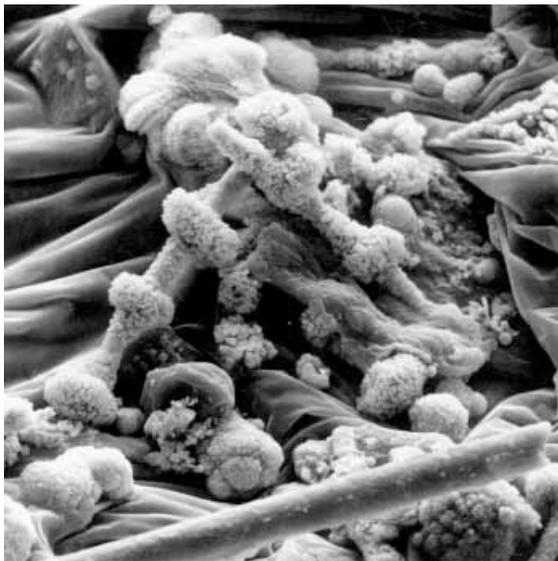


Fig. 33.5 SEM image of ferruginous bodies extracted from a human lung. Particles of asbestos are coated with an iron-rich material derived from proteins. (from Guthrie and Mossman, 1993; photograph by L. Smith and A. Sorling).

The fibrous scar tissue narrows the airways, causing shortness of breath.

The harmful effect of asbestos dust is in part dependent on the physical shape of the particles, and the fibrous morphology of asbestos is particularly detrimental. However, it appears that the relative ability of the body to dissolve these materials is also of key importance. Asbestos is much less soluble in the body than are nondisease-causing fibrous minerals. Equally significant is the surface chemistry and reactivity of the particles. For example, fresh surfaces of minerals, exposed by fracture, are highly reactive owing to the presence of under-coordinated surface atoms and broken bonds that accompany them. It has been observed that generation of free radicals by increased grinding of chrysotile fibers reduces the hemolytic activity because the particles become less crystalline. In chrysotile fibers enclosed in tissue, magnesium is preferentially leached from the fiber. If the surface chemistry of chrysotile is modified with polymers adsorbed to the particles, the toxic effect can be dramatically reduced.

As we have seen in Chapter 27, tetrahedral-octahedral sheets in chrysotile are rolled up similar to a scroll (see Figure 27.5). The outside of

the “scroll” is made up of the magnesium octahedral sheet, consisting of hydroxyl atoms on the surface that can be imaged with atomic force microscopy (AFM) (Figure 33.6). Each bright node in this image represents a hydroxyl on the surface, and each gray triangular region is a magnesium ion. It is on this surface that the chrysotile reacts with biological tissue. In the case of chrysotile, this surface is charge-balanced and fairly regular.

In the amphibole crocidolite, the surface is dominated by {110} cleavages parallel to the silicate chains. The surface structure is much more irregular, containing not only OH^- but also tetrahedral Si^{4+} , octahedral $\text{Mg}^{2+}/\text{Fe}^{2+}$, and larger cations (Ca^{2+} , Na^+). During dissolution, amphiboles become depleted in iron, sodium, calcium, and magnesium. If iron is oxidized during the leaching process, it reprecipitates as ferric oxyhydroxide. Analyses of leached crocidolite fibers in human tissue display amorphous surface layers. Because of these layers, crocidolite fibers have a much longer lifetime than chrysotile, and for this reason crocidolite is more pathogenic.

Exposure to quartz dust leads to *silicosis*, a progressive lung disease characterized by the development of scar tissue. Inhalation of quartz particles 0.5–0.7 μm in size causes proteins to develop that surround the particles, stimulat-

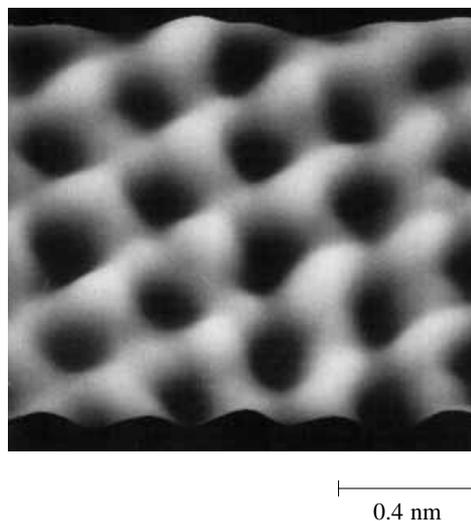


Fig. 33.6 AFM image showing the atomic arrangement in the surface of lizardite, with a hexagonal pattern of hydroxyl ions (bright spots) and magnesium ions in depressions (gray) (from Wicks et al., 1992).

ing fibroblast growth and producing collagen, an essential component of scar tissue. Fibrotic nodules develop in the region of small airways. As silicosis progresses, nodules coalesce and lesions develop that may involve one third of the lung, leading ultimately to respiratory failure. Silicosis has symptoms similar to those of asbestosis. Unlike asbestos exposure, however, there is no clear evidence for a relationship between lung cancer and silicosis.

Coal worker's *pneumoconiosis* is caused by fine-grained coal dust composed of carbonaceous material. Dust-laden cells form a mantle around respiratory bronchioles, which dilate as the mantle enlarges, causing emphysema. Pneumoconiosis often takes many years to develop and, unlike silicosis, there is often no progression of this disease in the absence of further exposure.

These lung diseases illustrate that the interaction of fibers with human tissue is very complex. Fibers with minor differences in composition and defect structure may have quite different biological activities. For example, glass fibers are not dangerous because they maintain their mechanical integrity and their dissolution rate is orders of magnitude faster than that of crystalline fibers.

Particle analysis

The assessment of hazardous concentrations of mineral particulates in the environment requires a combination of standardized industrial hygiene site-assessment techniques and mineralogical analytical procedures. We discuss these procedures in some detail because a fair number of mineralogists find employment in this field. The industrial hygiene assessment techniques typically involve a variety of sampling procedures (air drawn into membrane filters, wiping or vacuuming of known areas, direct sampling of building materials or rock/soil, etc.). The mineralogical procedures typically include the use of a polarized light microscope (PLM), phase contrast microscope (PCM), and transmission electron microscope (TEM) for asbestos, and X-ray diffraction (XRD) for quartz.

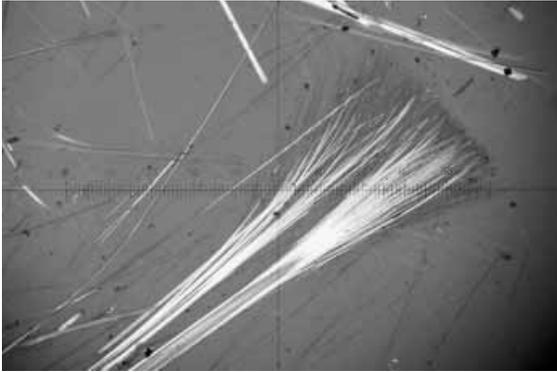
In the case of airborne particles, a known volume of air is collected onto a special type of membrane filter. Analysis of the particulate found on the filter is then performed using the appropriate technique. For asbestos air samples, a section

of an air filter is either (1) mounted on a glass slide and saturated with a special immersion oil for examination with a PLM or PCM or (2) prepared to create a carbon film replica of the filter surface for examination with a TEM. Figure 33.7a is a PLM image of amosite. Figure 33.7b and c are TEM images of amosite and chrysotile, respectively, each with a characteristic morphology. The number of fibers in a given area is counted and, if the volume of air sampled is known, the number of fibers per unit volume of air (measured as fibers per cubic centimeter) can be calculated. For example, in the USA the Occupational Safety and Health Administration (OSHA) has established a permissible time-weighted exposure limit for workers at 0.1 fibers per cubic centimeter of air during an 8 hour work day. Many other countries have similar regulations.

In the case of asbestos bulk samples of building materials and rock/soil samples, a different technique called optical polarized light microscopy is generally used. It involves taking a small sample of the bulk material, mounting it in immersion oil (see Chapter 10), and identifying the minerals present, quantifying the amount of asbestos by area estimate or by point count. It is a fairly straightforward, although tedious, technique, which gives good general data on mass quantities of asbestos.

A major limitation in the performance of asbestos analysis is the fact that asbestos fibers are considered to be hazardous down to a length of 0.5 μm , which is well below the resolution limit of optical microscopes. For the precise identification of the extremely small asbestos fibers, the TEM is the analytical method of choice, as it can easily resolve particles much smaller than 0.5 μm (Figure 33.7b,c). Furthermore the mineral identity of each individual asbestos fiber can be ascertained structurally by selected area electron diffraction (SAD) and chemically by energy dispersive X-ray analysis (EDXA).

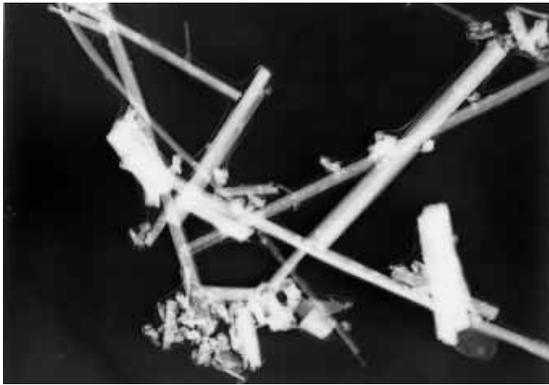
Commercial testing laboratories that perform asbestos analysis must be certified by government agencies to perform each specific type of test that they offer. To become certified, they must pass a detailed inspection of their facilities and pass proficiency tests whereby blind samples are submitted to their facilities. Such laboratories employ a substantial number of mineralogists



(a)



(b)



(c)

Fig. 33.7 Samples containing asbestos in airborne dust.
 (a) Polarized microscope sample of amosite (width 1.2 mm)
 (b) TEM image of amosite (width 6 μm) (c) TEM image of
 chrysotile (width 10 μm). (All micrographs are courtesy of
 Mark Bailey, Asbestos TEM Laboratories, Berkeley,
 California.)

to perform both optical and electron microscopy analyses.

Chemical contamination from mining

With the increasing industrialization of society, the demand for both metallic and non-metallic mineral products increases constantly. It is estimated that about 1.5 billion tonnes of rock mass are excavated each year during mining of mineral resources. This causes irreparable damage to the environment. Open pit mines expand and deepen; underground mining causes subsidence; dumps of waste rocks grow and tailings of ore-dressing plants expand; the atmosphere becomes polluted with gases from smelters, often enriched in SO_2 and CO_2 ; and natural water systems are also polluted. Soils in the vicinity of Sudbury in Canada, which is the world's largest nickel producer, have a pH of only 3 and this causes extensive loss of vegetation. Metals such as nickel, lead, and copper vaporize during the high temperatures of smelting and are dispersed over extensive areas surrounding the smelters (Figure 33.8).

The most important pollutant of the hydrosphere is H^+ , in the form of acid rain and acid mine drainage. Acid mine drainage results largely from the decomposition of pyrite to form iron hydroxide, H^+ and SO_4^{2-} . These reactions are often catalyzed by bacteria at low pH, increasing reaction rates by several orders of magnitude. Acid water produced by oxidation of sulfides can dissolve other metal sulfides and leach metals that are adsorbed in clays, thereby increasing the trace metal content in streams. Extremely low pH, even negative, never observed in natural systems, have been documented in mine waters in northern California (USA), and such acid waters have high concentrations of toxic metals such as arsenic, zinc, and cadmium.

Many industrialized countries have put severe limitations on mining operations to maintain some environmental standards. One of the first environmental mining laws was the prohibition of hydraulic mining in California (1860) to prevent erosion and destruction of fertile farmland. Today in the USA, groundwater must be protected during mining operations, requiring elaborate schemes to ensure such protection. In

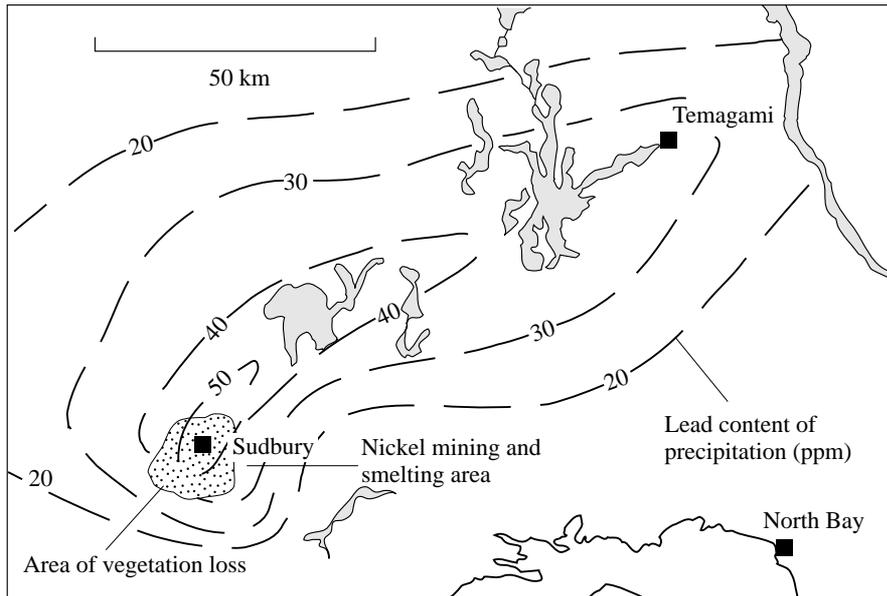


Fig. 33.8 Nickel content ($\mu\text{g/l}$) of atmospheric precipitation around Sudbury (Canada) recorded 1970–1974. The asymmetrical pattern is due to prevailing winds. Since then, the situation has much improved, but large concentrations of nickel and other heavy metal contaminants remain in soils. A zone of vegetation loss near Sudbury is shaded (after Semkin and Kramer, 1976).

addition, mines must be restored to a natural state after mining operations cease. This so-called “reclamation” is very costly, necessitating new efficient and effective technologies. Only a few years ago, the majority of mining mineralogists were engaged in prospecting and extraction technologies. Today many are conducting research into remediation of environmental damage. Modern mineral processing plants, at least in industrialized countries, must limit their emissions. The USA is the largest producer of SO_2 and CO_2 emissions from all sources combined, and emissions of SO_2 from mining and mineral processing still exceed 1000 tonnes per year. The result of such emissions is acid precipitation, which is prevalent in Eastern North America, Russia and many other parts of the world.

Whitton and Diaz (1980) documented worldwide a dramatic decrease in the number of photosynthetic organisms in rivers as zinc content

increased (Figure 33.9). Compounding the problem is that under anaerobic conditions, metal ions may form highly toxic organometallic complexes, such as methylated mercury (CH_3Hg^+). Natural waters acidified by mine drainage have killed enormous numbers of fish and benthic organisms and have made groundwater unsafe for human consumption. Geochemical reactions in mined areas are more rapid than in natural environments because of extensive exposures and large surface areas, particularly in tailings. It has been suggested that the effect of acid mine

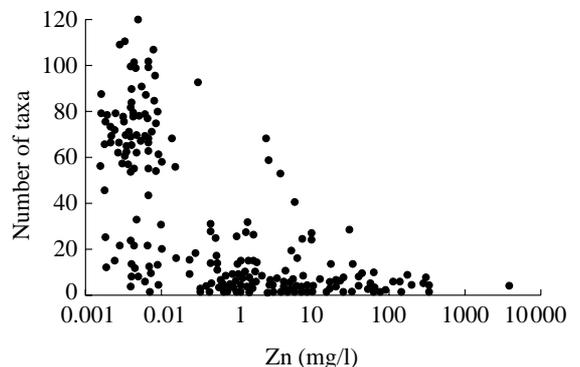


Fig. 33.9 Worldwide survey of the number of taxa of photosynthetic plants in stream water as function of the zinc content of the stream (after Kelly, 1999; see also Whitton and Diaz, 1980).

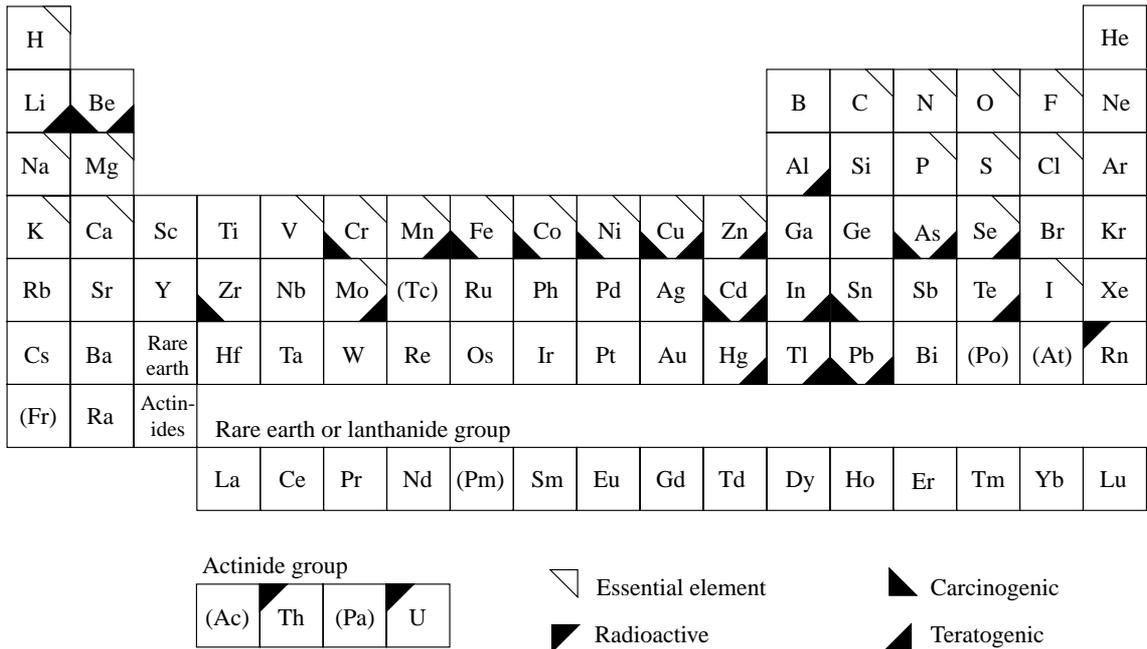


Fig. 33.10 Periodic system of elements, identifying those that are essential for human nutrition and those that are toxic and cause cancer (carcinogenic) or birth defects (teratogenic) if ingested in high doses. Also indicated are significant radioactive elements (after Smith and Huyck, 1999).

drainage is comparable to that of acid rain, owing to the atmospheric spread of industrial sources of acidification. It should be noted that mercury is not always a natural component of mining wastes but has been used extensively in gold extraction, in the process called amalgamation mentioned in Chapter 30. When this process was in extensive use, large amounts of mercury entered the atmosphere and rivers. Amalgamation was largely replaced by the environmentally more benevolent cyanide process in the early 1900s, but high concentrations of mercury are still present in soils around old mining districts, as well as in sediments of regions that receive the stream and river drainage of these districts. An example is San Francisco Bay in California, which received deposits from streams draining Sierra Nevada mining districts, more than 160 km away, during the Gold Rush period of the 1850s.

Figure 33.10 is a periodic system of elements on which the essential human nutrients are

marked, as well as toxic elements. The toxic elements are divided into those that are known to be carcinogenic, those that cause birth defects (teratogenic), and some that are radioactive. Among the radioactive elements, radon is most significant. It forms during radioactive decay of potassium, a major element in alkali feldspars, which are common in granitic rocks of continental shields.

Test your knowledge

1. List some mineral-like crystals that are found in the human body.
2. In health and nutritional sciences the definition of *mineral* is somewhat different from that in mineralogy. Explain the difference.
3. List some (“true”) minerals that are directly used in human nutrition.
4. Give examples of some elements that are essential for physiological functions but are toxic when used in larger doses.
5. Which minerals, if inhaled as particulate dust, are most hazardous to human health?
6. Review some of the dangers of acid mine drainage.

Important concepts

Minerals in the human body: apatite, calcite,
 Essential macroelements: Ca, Cl, Mg, P, K, Na, S
 Essential microelements: Cr, Co, Cu, F, Fe, I, Mn, Mo, Se, Zn
 Diseases related to mineral dust:
 Asbestosis (crocidolite, chrysotile)
 Lung cancer (crocidolite, chrysotile)
 Mesothelioma (crocidolite, chrysotile)
 Silicosis (quartz and silicates)
 Pneumoconiosis (coal)
 Chemical contamination (e.g., acid mine drainage)
 Carcinogenic elements: Be, Cr, Co, Ni, As, Zr, Cd, Pb
 Teratogenic: Li, Al, Mn, Cu, Zn, As, Se, Mo, Cd, In, Te, Hg, Tl, Pb

Further reading

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